

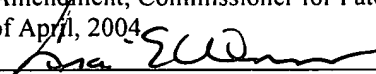
Docket No.: W0536-7005

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: James R. Graham, et. al.
Serial No: 10/014,848
Confirmation No: 1841
Filed: Dec. 11, 2001
For: ACTIVATED CARBON FOR ODOR CONTROL AND
METHOD FOR MAKING SAME
Examiner: Wayne A. Langel
Art Unit: 1754

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

The undersigned hereby certifies that this document is being placed in the United States mail with first-class postage attached, addressed to Mail Stop Non-Fee Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on the 5th day of April, 2004.



Signature

Mail Stop Non-Fee Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RULE 132 DECLARATION OF JAMES R. GRAHAM

I, James R. Graham, declare as follows:

1. I am an employee of United States Filter Corporation (US Filter), the Assignee of the above-identified application. I received a BS degree in chemistry from Indiana State University and a Ph.D. degree in inorganic chemistry from Iowa State University. I have been doing research and development work in the areas of surface chemistry and catalysis for over 35 years. For the past 15 years I have focused on the development of new products and process using activated carbon. During this time, I have extensively studied all types of activated carbons and their effectiveness in odor control applications. As Technical Director for US Filter, I have been responsible for conducting privately funded theoretical and experimental research in this area. For the past 6 years I have served as Chairman of the ASTM D-28 committee on activated carbon. This committee

is responsible for the development of standard test methods for the testing and characterization of activated carbons.

2. I am intimately familiar with activated carbon, its methods of manufacture, structure, composition and methods of characterization.

3. Adsorption by a porous material will be determined by its chemical composition and pore structure. Porosities of activated carbons are dependent not only on the starting materials used, but also on the activation methods and processes used in their preparation. (Influence of Activation Temperature on Micro-and Mesoporosity of Synthetic Activated Carbons, Park and Jung, Carbon Science, Vol. 2, No. 2, June 2001, pp 105-108.)

4. The micropore volume (the pore volume in pores less than 20 Angstrom units in diameter) of an activated carbon is measured by determining its butane number according to ASTM test method D5742. The micropore region is the portion of an activated carbon's pore structure where most of its surface area resides and where most adsorption and catalytic processes take place. A higher butane number indicates more internal pore volume is available for storage of reaction products resulting from oxidation of H₂S.

5. The ability of an activated carbon to sorb hydrogen sulfide is reported in grams of hydrogen sulfide adsorbed per cubic centimeter of carbon. This result is known as the hydrogen sulfide breakthrough capacity for the activated carbon. Hydrogen sulfide breakthrough capacity is determined using ASTM standard method D6646 by passing a moist stream of air containing 1 vol. % hydrogen sulfide through a one-inch diameter tube with a 9-inch deep bed of closely packed carbon at a rate of 1450 cc/min until a H₂S breakthrough concentration of 50 ppm is reached. This test method is extensively used by manufacturers and suppliers of odor control carbons to compare and contrast different materials for their ability to sorb hydrogen sulfide and then use this information to estimate their performance when used in field applications.

6. I have reviewed the specification of the above-identified application, the pending claims and the cited art.

7. Japanese Patent 7-313,867 (JP '867) discloses a method for making an odor control media that involves physically mixing a previously manufactured activated carbon with a metal oxide, an organic acid, methyl cellulose, and a clayey substance. The resultant mixture is kneaded and extruded.

8. I have prepared and tested a finished product according to the procedure disclosed in JP '867.

9. Embodiment 1 of JP '867 prepared, as described in the publication and with the following composition, has a butane number of 14.1% and a hydrogen sulfide breakthrough capacity of 0.07 gH₂S/ccC.

Active Carbon Powder	68 wt %
Metal Oxide (MgO)	14.6 wt %
Kaolin Clay	14.6 wt %
Methyl Cellulose	2.8 wt %

10. The activated carbon-metal oxide matrix of the present invention has a butane number of between about 24 % and about 26 %, and a hydrogen sulfide breakthrough capacity of greater than 0.25 gH₂S/ccC.

11. It is my opinion that the activated carbon-metal oxide matrix of the present invention shows a marked improvement in pore volume and hydrogen sulfide breakthrough capacity over the cited deodorant of JP '867, and that this significant improvement is unexpected.

12. It is also my opinion that the activated carbon-metal oxide matrix of the above-identified application is not disclosed in the reference and would not have been obvious to one of skill in the art of activated carbon. Although the cited art describes an activated

carbon and a metal oxide, it is really quite different than the present invention. The cited reference discloses and teaches forming a deodorant composition by mixing an activated carbon with a metal oxide leading to a deodorant where the metal oxide is deposited on the surface of the activated carbon within the pore structure of the finished product. The reference provides no teaching to one of skill in the art of preparing an activated carbon-metal oxide matrix wherein the metal oxide does not occupy and reduce the overall pore volume of the activated carbon.

13. All statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued therefrom.

Date: _____

4/05/2004

James R. Graham
James R. Graham

Influence of Activation Temperature on Micro- and Mesoporosity of Synthetic Activated Carbons

Soo-Jin Park[✉] and Woo-Young Jung

Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejeon 305-600, Korea

[✉]e-mail: psjin@kriict.re.kr

(Received April 16, 2001; accepted April 30, 2001)

Abstract

In this work, the activated carbons (ACs) with high micropores were synthesized from the polystyrene (PS) with KOH as activating agent. And the influence of activation temperature on porosity of the ACs studied was investigated. The porous structures of ACs were characterized by nitrogen adsorption at 77K using BET and D-R equations, and MP and BJH methods. The weight loss behaviors of the samples impregnated with KOH were also monitored using thermogravimetric analyzer (TGA). As a result, it was found that the samples could be successfully converted into ACs with well-developed micropores. From the results of pore size analysis, it was confirmed that elevated activation temperature does lead to the formation and deepening of microstructures without significant change in mesostructures. A thermogravimetric study showed that KOH could suppress the thermal decomposition of the sample, resulting in the increase of carbon yields.

Keywords : Activated carbons, Chemical activation, Potassium hydroxide, Decomposition, Micro- and mesoporosity

1. Introduction

Activated carbons (ACs) have been extensively used as adsorbents, catalysts, and catalyst supports for the removal of pollutant species from gases or liquids and for purification or recovery of chemicals [1, 2]. The usefulness of these carbons arises not only from their structural parameters, such as the specific surface area and the total pore volume, but also from the presence of functional groups on the surface [3-5]. It is well known that ACs can be prepared from a wide range of carbonaceous materials with a high carbon content and low levels of inorganic compounds [6-8]. The most frequently used materials are coal, wood, and coconut shell in the commercial ACs. Recently, there are a quite large number of studies regarding the preparation of ACs from various polymeric materials because of high carbon yield and low ash content [9-13].

Porosities of ACs are dependent not only on the starting materials, but also on the activation methods and processes. The processes for the preparation of activated carbons can be generally divided into two categories: physical and chemical activations. Physical activation involves carbonization of the raw materials followed by gasification of the resulting char in the presence of some oxidizing agents, such as steam [14] or carbon dioxide [15]. On the other hand, chemical activation is performed by the thermal decomposition of the precursor materials impregnated with chemical agents, such as, potassium hydroxide [6, 16], zinc chloride [17], and phosphoric acid [18]. In the chemical activation, all the chemicals

used act as dehydrating agents that promote the formation of cross-links, resulting in the formation of rigid matrix that will be less susceptible to volatile loss and volume contraction upon pyrolysis process [6]. Therefore, the advantage of chemical activation is that temperature of process to be lower since carbon burn-off is not required.

In chemical activation process, one of the variables having a larger effect on the porosity of the final carbons is the activation temperature. Thus, the main objectives of the present work is to prepare activated carbons from polymeric materials by chemical activation with potassium hydroxide and to study the effect of activation temperatures on the structural properties of the final activated carbons. Also, the decomposition and carbon yield behaviors during activation are investigated using thermogravimetric analyzer (TGA).

2. Experimental

2.1. Materials and Sample Preparation

Polymeric materials based on polystyrene (PS) and potassium hydroxide (KOH) were used as the starting material and chemical agent, respectively. The materials were added to a KOH solution and then, the mixture was gently stirred at 100°C for 3 h to ensure a complete reaction between KOH and PS. The concentration of the KOH solution was adjusted to give KOH to PS ratio of 0.5 by weight. After mixing, the mixture was dried at 110°C for 24 h. The samples were placed in a quartz combustion boat and loaded into a hori-

zontal cylindrical furnace (ID=60 mm) in a nitrogen atmosphere, with a flow rate of 150 ml/min. Pyrolysis was carried out by heating the samples at 5°C/min, followed by retaining for 2 h at activation temperatures (700, 800, and 900°C) in furnace. After cooling, the products were crushed using a mortar and pestle to obtain particle sizes smaller than 600 μm . The crushed samples were washed sequentially with 0.5 N HCl solution at 100°C, boiling water, and finally cold distilled water to remove residual organic and mineral matters, then dried at 110°C for 24 h.

2.2. Characterization of Activated Carbons

The adsorption isotherms of N_2 were measured on the ACs studied at 77 K using an ASAP 2010 (Micromeritics). Prior to the analysis, the samples were outgassed at 298 K for 6 h to obtain a residual pressure of less than 10^{-3} torr. The BET equation was used to calculate the specific surface area (S_{BET}) from the amount of nitrogen adsorbed on ACs [19]. The total pore volume (V_T) was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.995. The micropore volume (V_{micro}) was calculated using the Dubinin-Radushkevich (DR) equation [20], and the mesopore volume (V_{meso}) was obtained by subtracting the micropore volume from the total pore volume. The average pore diameter was measured by dividing the specific surface area with the total pore volume. Also, the MP method [21] and the BJH model [22] were used to investigate micropore and mesopore size distribution, respectively.

2.3. Thermogravimetric Analysis

The weight loss behavior of the ACs studied was monitored using thermogravimetric analyzer (TGA, DuPont TGA-2950). The samples were heated from 30 to 800°C at a heating rate of 20°C/min.

3. Results and Discussion

3.1. Nitrogen Adsorption Isotherms

It is well known that the activation temperature is one of the important parameters in the preparation of ACs using the chemical activation method [6]. Fig. 1 shows nitrogen adsorption isotherms of the ACs prepared at different activation temperatures with a carbonization time of 2 h. The KOH to PS ratio was fixed at 0.5. It is clearly shown that the shape of the nitrogen adsorption isotherms is very similar with each other and is shifted upward due to the difference in their adsorption capacities, suggesting similarity in the pore structure [23]. All of the adsorption isotherms exhibit a sharp Type I isotherm, according to the BETs classification [19]. Major uptake occurs at low relative pressures of less than 0.1 and the plateaus are fairly horizontal. It is then noted that the formation of highly microporous materials with narrow pore size distribution is established in the ACs studied.

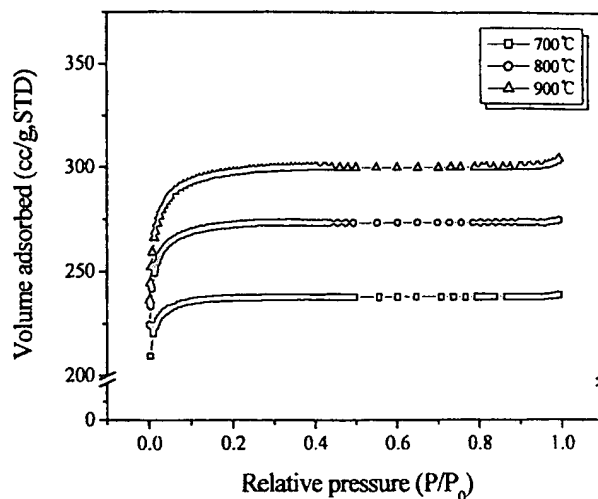


Fig. 1. Nitrogen adsorption isotherms at 77 K for the ACs studied at different activation temperatures.

Table 1. Structural parameters of the ACs studied

Nomenclature	S_{BET} [m^2/g]	V_T [cm^3/g]	V_{mi} [cm^3/g]	D_p [\AA]
700°C	985	0.39	0.38	15.8
800°C	1,105	0.43	0.43	15.6
900°C	1,198	0.47	0.47	15.7

Table 1 summarizes the structural parameters at different activation temperatures determined from the nitrogen adsorption isotherms according to the BET and D-R equations. It is shown that the BET's surface area and the total pore volume increase as the activation temperature increases. The BETs surface area and the total pore volume are as high as 1198 m^2/g and 0.47 cm^3/g , respectively. It implies that ACs with a well-developed porosity could be prepared from KOH-impregnated PS and an increase in the activation temperature results in the production of ACs with high BETs surface area and total pore volume. However, the average pore diameters of the ACs treated by KOH do not significantly change as the activation temperature increases. It is probably due to the formation of new micropores and/or the deepening of the existing micropores.

To clarify the changes in the microporous and mesoporous structure of the ACs studied, the pore size distributions are evaluated by MP and BJH methods, respectively. Micropore analysis by the MP method is based on the t -plot in which the adsorbed volume of the adsorbate is plotted against the thickness of adsorbed layer, t , starting from $t=3.5 \text{ \AA}$. The t as a function of P/P_0 was calculated from the Harkins and Jura equation [24]. Fig. 2 shows the micropore size distributions as functions of activation temperatures. It shows that all pore distribution curves of the ACs studied have one peak with maximum density at less than 4 \AA in radius, and the pore

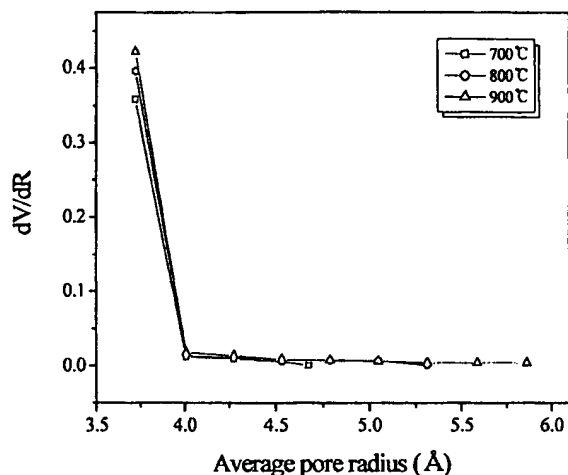


Fig. 2. Micropore size distributions for the ACs studied.

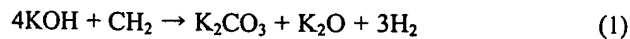
size distribution is very narrow. Also, the height of peaks representing the adsorption pore volume increases with increasing the activation temperature without shifting to the larger pore size. As mentioned above, it is expected that the formation of new micropores and/or the deepening of the existing micropores affect the estimated value of the average pore diameter.

Fig. 3 presents the distributions of pore size determined from BJH method. As a result, the development of the mesoporous structure was not observed. It is clearly noted that there is no widening of porosity with increasing the activation.

3.2. Thermogravimetric Analysis

Although a lot of works have been done in the area of chemical activation, the mechanism of process has not well established yet. TGA measurement was done to investigate the variation of mechanism with the addition of KOH into PS.

The results of TGA of the samples are shown in Fig. 4. It is seen that KOH-loaded PS undergoes decomposition in two steps while the as-received sample decomposes in a single step. As illustrated in Fig. 4(a), it can be clearly seen that the sample is rapidly decomposed around 480°C where the weight is almost lost. While, the decomposition of KOH-loaded PS is greatly suppressed as seen in Fig. 4(b), resulting in no significant decrease of carbon yield as the temperature increases. As shown in equation (1), it can be probably considered due to the substitution of H groups in PS structures with OK in the reagents during the interaction between KOH and PS [25, 26].



A primary char is formed in the first step that is completed around 490 and undergoes further decomposition at higher temperatures in the second step. It is also shown that the

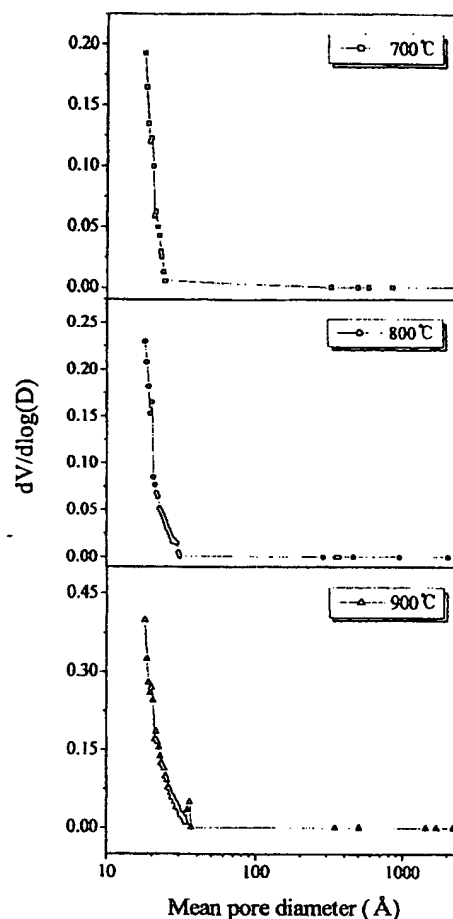


Fig. 3. BJH pore size distributions for the ACs studied.

weight of sample slightly decreases with the increase of the temperature from 500 to 800°C. It is largely attributed to carbon gasification by the released CO_2 from K_2CO_3 and K_2O formed during carbonization below 500°C [27]. The released CO_2 can react with carbon atoms in PS to open up closed pores and deepening the existing micropores. In addition to the gasification by the released CO_2 , potassium-containing compounds, such as, K_2CO_3 and K_2O can be reduced by carbon to form K metal [7, 27, 28], thus causing carbon gasification, as well as oxidation. Reaction of these compounds with carbon atoms can be as follow:



To investigate the effect of activation temperature on carbon yield, the yield of the ACs studied is calculated using the following equation (4):

$$\text{Carbon yield (in wt\%)} = [W_1/W_2] \times 100 \quad (4)$$

where, W_1 and W_2 are the weights of the activated carbon product and the KOH-loaded PS, respectively.

Fig. 5 shows the effect of activation temperature on carbon

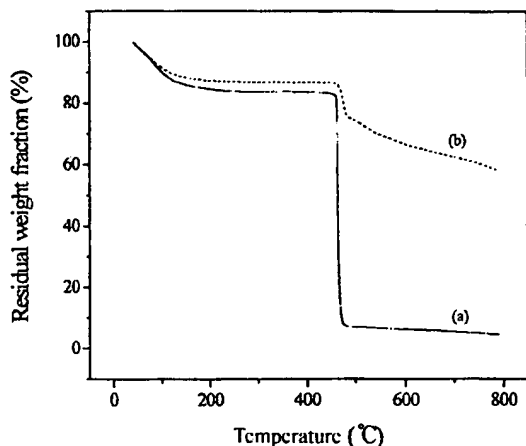


Fig. 4. TGA thermograms for (a) as-received and (b) PS loaded with KOH.

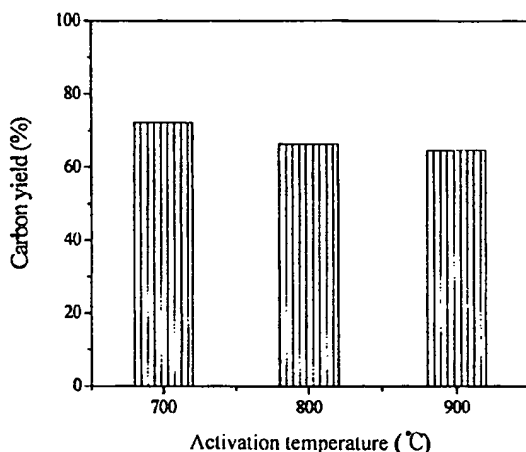


Fig. 5. Effect of carbonization temperature on carbon yield of the ACs studied.

yield of KOH-loaded PS. It can be seen that the carbon yield decreases as the activation temperature increases. As mentioned above, it is attributed to the fact that potassium-containing compounds, such as K_2CO_3 and K_2O formed at low temperatures are the active sites in gasification, leading to a decrease in carbon yield at high temperatures.

4. Conclusion

Activated carbons (ACs) with microporous structure were prepared by chemical activation from polymeric materials based on polystyrene (PS) with KOH as activating agent. As the activation temperature increases, the formation and deepening of new micropore are observed without widening in micropores or significant change in mesoporosity. From the results of TGA, it is confirmed that KOH played an important role in the development of micropore and the increase of carbon yield.

Acknowledgement

This work was supported by grant No. 2000-2-30100-011-3 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

- [1] Cheremisinoff, P. M.; Ellerbusch, C. *Carbon Adsorption Handbook*, Ann Arbor Science, Ann Arbor, Michigan, 1978.
- [2] Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*, Dekker, New York, 1988, 27.
- [3] Park, S. J.; Park, B. J.; Ryu, S. K. *Carbon* **1999**, *37*, 1223.
- [4] Park, S. J.; Kim, K. D. *J. Colloid Interface Sci.* **1999**, *212*, 186.
- [5] Park, S. J.; Donnet, J. B. *J. Colloid Interface Sci.* **1998**, *200*, 46.
- [6] Hsu, L. Y.; Teng, H. *Fuel Process. Technol.* **2000**, *64*, 155.
- [7] Ahmadi, A.; Do, D. D. *Carbon* **1997**, *35*, 1723.
- [8] Wartelle, L. H.; Marshall, W. E. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 451.
- [9] Kruk, M.; Jaroniec, M.; Gadkaree, K. P., *J. Colloid Interface Sci.* **1997**, *192*, 250.
- [10] Martinez-Alonso, A.; Jamond, M.; Montes-Moran, M. A.; Tascon, J. M. D. *Microporous Mater.* **1997**, *11*, 303.
- [11] Choma, J.; Jaroniec, M. *Langmuir* **1997**, *13*, 1026.
- [12] Puziy, A. M. *Langmuir* **1995**, *11*, 543.
- [13] Marzec, M.; Tryba, B.; Kalenczuk, R. J.; Moarowski, A. W. *Polym. Adv. Technol.* **1999**, *10*, 588.
- [14] Klose, E.; Born, M. *Fuel* **1985**, *64*, 1313.
- [15] Laine, J.; Yunes, S. *Carbon* **1992**, *30*, 601.
- [16] Otowa, T.; Nojima, Y.; Miyazaki, T. *Carbon* **1997**, *33*, 1105.
- [17] Khalili, N. R.; Campbell, M.; Sandi, G.; Golas, J. *Carbon* **2000**, *38*, 1905.
- [18] Benaddi, H.; Bandoz, T. J.; Jagiello, J.; Schwarz, J. A.; Rouzaud, J. N.; Legras, D.; Beguin, F. *Carbon* **2000**, *38*, 669.
- [19] Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
- [20] Dubinin, M. M. *Chem. Rev.* **1960**, *60*, 235.
- [21] Mikhail, R. S.; Brunauer, S.; Bodor, E. E. *J. Colloid Interface Sci.* **1968**, *26*, 45.
- [22] Barrett, E. P.; Joyner, L. C.; Halenda, P. H. *J. Am. Chem. Soc.* **1951**, *73*, 373.
- [23] Bagreev, A.; Adib, F.; Bandoz, T. J. *J. Colloid Interface Sci.* **1999**, *219*, 327.
- [24] Harkins, W. D.; Jura, G. *J. Chem. Phys.* **1943**, *11*, 431.
- [25] Yamashita, Y.; Ouchi, K. *Carbon* **1982**, *20*, 43.
- [26] Hayashi, J.; Kazehaya, A.; Muroyama, K.; Watkinson, A. P. *Carbon* **2000**, *38*, 1873.
- [27] Illan-Gomez, M. J.; Garcia-Garcia, C.; Salinas-Martinez de Lecea, C.; Linares-Solano, A. *Energy Fuels* **1996**, *10*, 1108.
- [28] Hu, Z.; Vansant, E. F. *Carbon* **1995**, *33*, 1293.